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THE USE OF BROMINE TRIFLUORIDE IN THE RECOVERY OF URANIUM FROM MIXTURES OF UO$_2$ AND MgO

By
F. D. Rosen

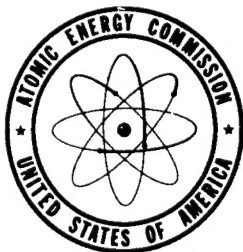*DTIC QUALITY INSPECTED 2*

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THE USE OF BROMINE TRIFLUORIDE
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PREPARED BY:

F. D. ROSEN

ATOMIC ENERGY RESEARCH DEPARTMENT

NORTH AMERICAN AVIATION, INC.

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ABSTRACT

A method is described for recovery of uranium from $UO_2 \cdot MgO$ ceramic fuel material by the use of bromine trifluoride. Recovery of 99.8 per cent uranium from pressed-sintered $UO_2 \cdot MgO$ was accomplished by grinding the material to 6 micron particle size, wetting with bromine and boiling with BrF_3 for 3 hours. A study of particle size vs uranium recovery was made.

This report is based upon studies conducted for the Atomic Energy Commission under Contract AT-11-1-GEN-8.

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I. INTRODUCTION

The proposed use of ceramic type fuel elements in power reactors has made the study of uranium recovery from ceramic materials of interest.

Fluoride volatility processes for uranium recovery have been applied to metallic uranium,[1,2] uranium impregnated graphite[3] and uranium-zirconium alloy.[4] The work described in this report was performed to show the adaptability of a fluoride volatility process to the recovery of uranium from nuclear fuels of a ceramic type.

A ceramic material composed of UO_2 and MgO was selected for this study.

Emeleus and co-workers[6] have shown that uranium oxides react quantitatively with BrF_3 to produce UF_6. The presence of MgO in the material, however, was expected to inhibit the reaction, since MgO reacts incompletely with BrF_3.[7] In this work uranium recovery was studied by treating samples of $UO_2 \cdot MgO$ ceramic with boiling BrF_3. The efficiency of recovery was determined by uranium analysis for the UF_6 produced and of the residue which remained after reaction. Uranium decontamination was not studied, since separation of UF_6 from fission products has been demonstrated at the Argonne National Laboratory[1] and the Brookhaven National Laboratory.[8]

The efficiency of uranium recovery from $UO_2 \cdot MgO$ ceramic was dependent on the history of the material prior to BrF_3 treatment. An average recovery of 99.7 per cent was obtained on material which had not been pressed prior to sintering. On material which had been cold pressed at 10,000 psi and sintered at 1800° C, an average recovery of 98 per cent was observed. Grinding the samples to 6 micron average particle size increased the efficiency of recovery to 99.8 per cent. By treatment of samples of various particle size with BrF_3, an empirical relationship between particle size and uranium recovery was determined.

II. EXPERIMENTAL

A. Apparatus

An apparatus was designed to permit the following:

1. Treatment of $UO_2 \cdot MgO$ samples with boiling BrF_3 at near atmospheric pressure
2. Condensation of the volatilized BrF_3 and its return to the reaction mixture
3. Separation of the UF_6 formed from BrF_3
4. Quantitative collection of the UF_6 in a form convenient for chemical analysis
5. Absorption of all corrosive gases
6. Control of pressure in the system at just below atmospheric to prevent loss of UF_6 due to leaks

The apparatus used was similar to that described by Gardner[9] and is shown schematically in Fig. 1.

The reaction tube was made from 15 millimeter Vycor tubing and was heated electrically. Bare, 20 gauge nichrome wire was used as the heating element to allow visual observation of the sample during reaction. Heat input to the reaction tube was controlled by means of a 6 volt transformer and variac. A Teflon connector and two steel springs joined the reaction tube to the reflux tube which was also constructed of 15 millimeter Vycor. The UF_6 absorber was made of 25 millimeter Vycor and was connected to the reflux tube by means of a 29/42 standard taper Vycor joint and a short length of 9 millimeter Vycor tubing. Reagent grade boric acid crystals were used as the absorbing material and were found to be very effective for the quantitative removal of UF_6 from a gas stream. A standard Pyrex absorption bulb filled with technical grade soda-lime served as the absorber for bromine and any other corrosive gases not removed by the boric acid. Tygon tubing, 3/8 inch OD, was used to join the bromine absorber to the apparatus. A Pyrex manostat filled with Octoil served as a pressure controller. Pressure was regulated between 742 and 760 millimeters Hg by means of the leveling bulb. The flow rate of air through the manostat was manually controlled by a valve leading to a Wetch Duo-seal vacuum pump.

B. Procedure

A typical UF_6 recovery run is described below.

A weighed sample of $UO_2 \cdot MgO$ having a known uranium content was placed in the detached reaction tube. The sample was covered with a minimum amount
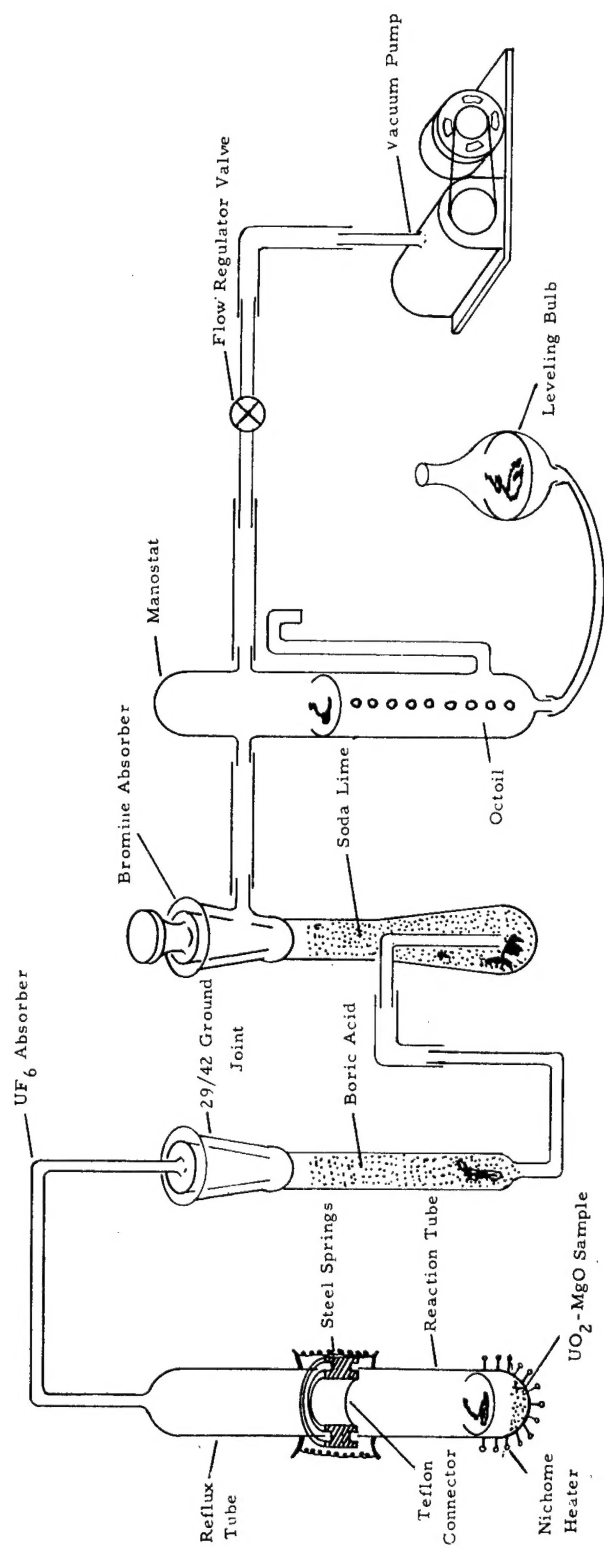
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Figure 1.

Apparatus for Reaction of BrF_3 with $UO_2 \cdot MgO$

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of liquid bromine and the mixture frozen by immersing the end of the tube in liquid nitrogen. Bromine trifluoride, approximately 5 grams, was added to the reaction tube which was still in the liquid nitrogen bath. After the BrF_3 had frozen, the tube was removed from the cold bath and quickly replaced on the apparatus. The freezing was necessary in order to prevent the loss of UF_6 while the reaction tube was being attached to the system. The presence of bromine also served to control the rate of reaction which would have been too rapid when fuel samples of small particle size were used.

Immediately after the reaction tube had been replaced on the apparatus, the vacuum pump was started and the regulator valve opened to allow a rapid bubble rate of air through the manostat. A vacuum of about 10 inches of oil was set with the leveling bulb (1 inch of oil = 1.8 millimeters of Hg).

As the frozen mixture of bromine and sample began to melt, the reaction started and proceeded smoothly. After the BrF_3 had melted and the reacting mixture had warmed to room temperature the nichrome heater was placed on the reaction tube and low voltage applied until the mixture boiled. The voltage was gradually increased until rapid boiling and refluxing were observed in the reaction tube; this caused the sample to be in a state of agitation in the BrF_3. Bromine and UF_6 slowly distilled out of the reaction tube into the reflux tube and finally into the absorption traps. Small amounts of BrF_3 vapors were also carried into the absorption train where they reacted easily with the boric acid and presented no difficulty. At this time the vacuum in the system was reduced to about 3 inches of oil, and boiling continued for the specified time.

After the reaction period had expired, the reaction tube was removed from the apparatus and the BrF_3 distilled off into a fume hood, leaving behind a dry residue. The weight of uranium retained by the residue was determined by dissolving it in concentrated HNO_3 and analyzing for uranium fluorometrically. The visual comparison method described by Grimes and Clark[10] was used.

The reflux tube and the contents of the UF_6 absorber were washed into a platinum dish and evaporated to dryness after addition of excess HF and H_2SO_4. This process removed all boron and fluorine compounds from the sample and allowed a volumetric analysis for uranium to be made without further separation. The method of collecting UF_6 in boric acid and subsequent analysis was developed and described in detail by Gardner.[9]

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After the initial experiments, a fluorometric analysis was made of the material in the bottom of the soda-lime trap. No uranium was found.

In the experiments in which UF_6 was not collected, the procedure was the same as described above, except that the absorption train was not used and the reaction was carried out at atmospheric pressure. Uranium recovery in these experiments was based only on analysis of the residue.

C. Materials

Four preparations of $UO_2 \cdot MgO$ ceramic materials were made. All materials contained approximately 68 per cent by weight UO_2 and 32 per cent by weight MgO.[5] The UO_2 used was obtained from the Mallinckrodt Chemical Works. Analytical reagent grade MgO was used.

In the first preparation, UO_2 and MgO were ground together with a mortar and pestle and hand packed into a molybdenum crucible. The crucible was then heated by induction to 2000° C in an atmosphere of helium. A hard, black ceramic was formed which had to be drilled out of the crucible. X-ray diffraction analysis of this material showed only UO_2 and MgO to be present. Upon treatment with BrF_3, however, it became apparent that this material was contaminated with molybdenum.

The second preparation differed from the first in that a tantalum crucible was used and heated to 1900° C. Material resulting from this operation was found to be contaminated with tantalum.

For the third preparation, the mixed powders were cold pressed into a small pellet and sintered at 1800° C in a vacuum resistance furnace. The pellet was supported by a layer of MgO powder placed on a graphite disc. This method of preparation was satisfactory except that some uranium was lost, presumably by vaporization. Post-run analysis of the graphite disc showed 1 milligram of uranium.

In the procedure used for the fourth preparation, the UO_2 and MgO mixture was ground and cold pressed at 10,000 psi into a pellet approximately 1 inch in diameter by 1/2 inch high. The pellet was placed in a graphite crucible on a layer of MgO powder. "Bubble" zirconia* was used to insulate and support the

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*Made by the Norton Company.

crucible in a 4 inch fused quartz tube. The crucible was heated by induction to 1800° C in an atmosphere of helium. During the sintering operation, the density of the pellet increased approximately from 3 to 6 gm/cm^3. The sintered pellet was ground, with difficulty, in a mortar and pestle. A sample of the resulting powder was found by X-ray analysis to contain only UO_2 and MgO. Chemical analysis of the powder showed 56.4 per cent by weight uranium. Part of the powder was classified by screening into three fractions containing particles averaging 500, 100 and 50 microns in size. Another fraction of 6 microns average particle size was prepared by grinding and elutriation in carbon tetrachloride. Particle size of this fine powder was determined microscopically with the aid of a calibrated eyepiece. Chemical analysis of the 6 micron powder showed 57.1 per cent by weight uranium.

The BrF_3 used in this work was obtained from Foltz[11] and had been purified by distillation. The bromine used was reagent grade material.

III. RESULTS AND DISCUSSION

The controlling factor in the recovery of uranium from $UO_2 \cdot MgO$ ceramic materials was found to be the treatment of the materials prior to reaction with BrF_3. For this reason, the data are divided into Tables I through V according to the method of preparation of the samples.

Two methods were used to evaluate the efficiency of uranium recovery: recovery based on analysis of the residue and recovery based on analysis of the uranium collected in the UF_6 absorber.

Recovery based on analysis of the residue or the per cent of uranium removed from the sample was calculated by means of Eq. (1).

$$\% \text{ recovery} = 100 \left(1 - \frac{W_r}{W_o}\right) \qquad \ldots (1)$$

where

W_r = grams of uranium found in the residue,
W_o = grams of uranium initially present in the sample.

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Recovery based on analysis of the uranium collected was calculated by means of Eq. (2).

$$\% \text{ recovery} = 100 \ \frac{W_c}{W_o} \qquad \qquad \ldots(2)$$

where

$$W_c = \text{grams of uranium found in the } UF_6 \text{ absorber.}$$

If it is assumed that no uranium is lost during the experiment and that the analytical results are free from error, then $W_r + W_c = W_o$; and the per cent recovery calculated by both methods would be the same. However, the estimated error in the analyses for uranium collected was ± 1 per cent, and an error of ± 25 per cent has been assumed in the residue analyses (Grimes and Clark[10] gave ± 15 per cent). Therefore, since values of uranium recovery in the range near 99.9 per cent were of greatest interest, a ± 1 per cent error in the analysis of the uranium collected would make the recovery value obtained by Eq. (2) lie between 98.9 and 100.9 per cent. On the other hand, a ± 25 per cent error in the residue analysis would yield a value obtained by Eq. (1) lying between 99.925 and 99.875. Thus in cases where recovery was high, those results calculated by Eq. (1) are more significant.

Table I shows results obtained from preliminary experiments on unsintered mixtures of UO_2 and MgO powders. The high uranium recovery obtained in these experiments indicates that the presence of MgO had no chemical effect on the conversion of UO_2 to UF_6. In addition, these results show that the apparatus and procedure used would permit a quantitative separation and transfer of uranium from the reaction mixture into the absorption trap.

The results presented in Table II show that high uranium recovery was obtained from materials which had not been pressed but only sintered at 1900 to 2000° C. It is suspected that the results obtained in this group of experiments may have been affected by the presence of metallic impurities in the $UO_2 \cdot MgO$ samples. These impurities came from the metal crucibles in which the ceramics were fired.

Table III shows the results obtained on $UO_2 \cdot MgO$ ceramic material which was prepared by cold pressing and sintering. This method of preparation was

used in order to simulate the condition of a fuel mixture after having been re-moved from an operating reactor. The 98 per cent average uranium recovery observed in this series of experiments may be explained by assuming the unre-moved uranium to be protected by an impervious coating of MgO formed during the pressing and sintering operation. Prolonged reaction with BrF_3 was tried in two experiments but gave no increase in the per cent uranium removed. In two other experiments, the residue from an initial BrF_3 treatment was taken from the reaction tube, ground to a fine powder and treated again with BrF_3. This second treatment removed an additional 25 per cent of the unreacted urani-um.

In an effort to improve the recovery of uranium from pressed-sintered material, a study of the effect of particle size on uranium recovery was made. The results of this study are presented in Table IV and Fig. 2. The fact that uranium recovery increased as particle size was reduced strengthens the hypothesis that some of the uranium was protected by a coating impervious to BrF_3. The relationship between particle size and per cent uranium recovery shown in Fig. 2 may be expressed by the following empirical relation:

$$x = 100 - \frac{d^{0.73}}{19} \qquad \qquad \ldots(3)$$

where

x = weight per cent uranium recovery

d = average particle size in microns.

Table V shows the results of three experiments made to demonstrate ef-ficient recovery of uranium from pressed and sintered $UO_2 \cdot MgO$. The poor re-sult obtained in one of the experiments was due to a small leak of UF_6 which was observed during the initial part of the run. These results are also plotted in Fig. 2. Analysis of the residue from one of these runs for fluoride showed that only about 10 per cent of the MgO had been converted to MgF_2.

IV. CONCLUSION

Bromine trifluoride may be used for the quantitative recovery of uranium from $UO_2 \cdot MgO$ ceramic material. When the $UO_2 \cdot MgO$ has been pressed and

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sintered, it is necessary to grind the material to a fine particle size prior to treatment. The reaction rate of BrF_3 with finely ground $UO_2 \cdot MgO$ is too rapid for practical use and is moderated by the addition of bromine.

No accidents or hazardous situations were encountered during this work.

TABLE I

RECOVERY OF URANIUM FROM UNPRESSED UNSINTERED $UO_2 \cdot MgO$ POWDER MIXTURE

Sample Wt gm	Wt U gm	Reaction Time hr	Wt U Found in Residue gm	Wt U Collected gm	% Recovery Based on Residue	% Recovery Based on U Collected	% U Accounted For
0.126	0.0760	2.09	1×10^{-6}	0.0767	>99.9	100.9	100.9
0.136	0.0819	2.5	1×10^{-6}	0.0825	>99.9	100.7	100.7

TABLE II

RECOVERY OF URANIUM FROM UNPRESSED SINTERED $UO_2 \cdot MgO$

Sample Preparation	Sample Wt gm	Wt U gm	Reaction Time hr	Wt U Found in Residue gm	% U Recovery Based on Residue
Heated to 2000° C in molybdenum crucible	0.336	0.212	4	0.0004	99.8
Heated to 2000° C in molybdenum crucible	0.155	0.0976	3	0.0003	99.7
Heated to 2000° C in molybdenum crucible	0.0718	0.0453	3	0.00002	99.9
Heated to 1500° C in tantalum crucible	0.252	0.159	10	0.0011	99.3

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TABLE III

RECOVERY OF URANIUM FROM COLD PRESSED-SINTERED $UO_2 \cdot MgO$

Sample Preparation	Sample Wt gm	Wt U gm	Reaction Time hr	Wt U Found in Residue gm	% U Recovery Based on Residue
Cold pressed at 10,000 psi Sintered at 1800° C in helium atmosphere	1.915	1.155	16	0.0118	99.0*
	3.276	1.848	3	0.0355	98.1†
	0.147	0.083	19	0.0032	96.2
	0.562	0.317	3	0.0069	97.8
	Residue ground and retreated	0.338	3	0.0056	98.2
	0.598		3	0.0071	97.9
	Residue ground and retreated		3	0.0051	98.5

*Recovery based on U collected was 98.7 per cent.

†Recovery based on U collected was 96 per cent.

TABLE IV

EFFECT OF PARTICLE SIZE ON THE RECOVERY OF URANIUM FROM UO$_2$·MgO COLD PRESSED-SINTERED MATERIAL*

Average Particle Size microns	Sample Wt gm	Wt U gm	Wt U Found in Residue gm	% U Recovery Based on Residue
500	0.292	0.159	0.008	95.0
100	0.252	0.142	0.0021	98.5
50	0.181	0.102	0.0008	99.2
6	0.362	0.204	0.0003	99.85

*This material was cold pressed at 10,000 psi and sintered at 1800° C. The reaction time for all experiments was 3 hours.

TABLE V

RECOVERY OF URANIUM FROM COLD PRESSED-SINTERED UO$_2$·MgO CERAMIC GROUND TO 6 micron AVERAGE PARTICLE SIZE

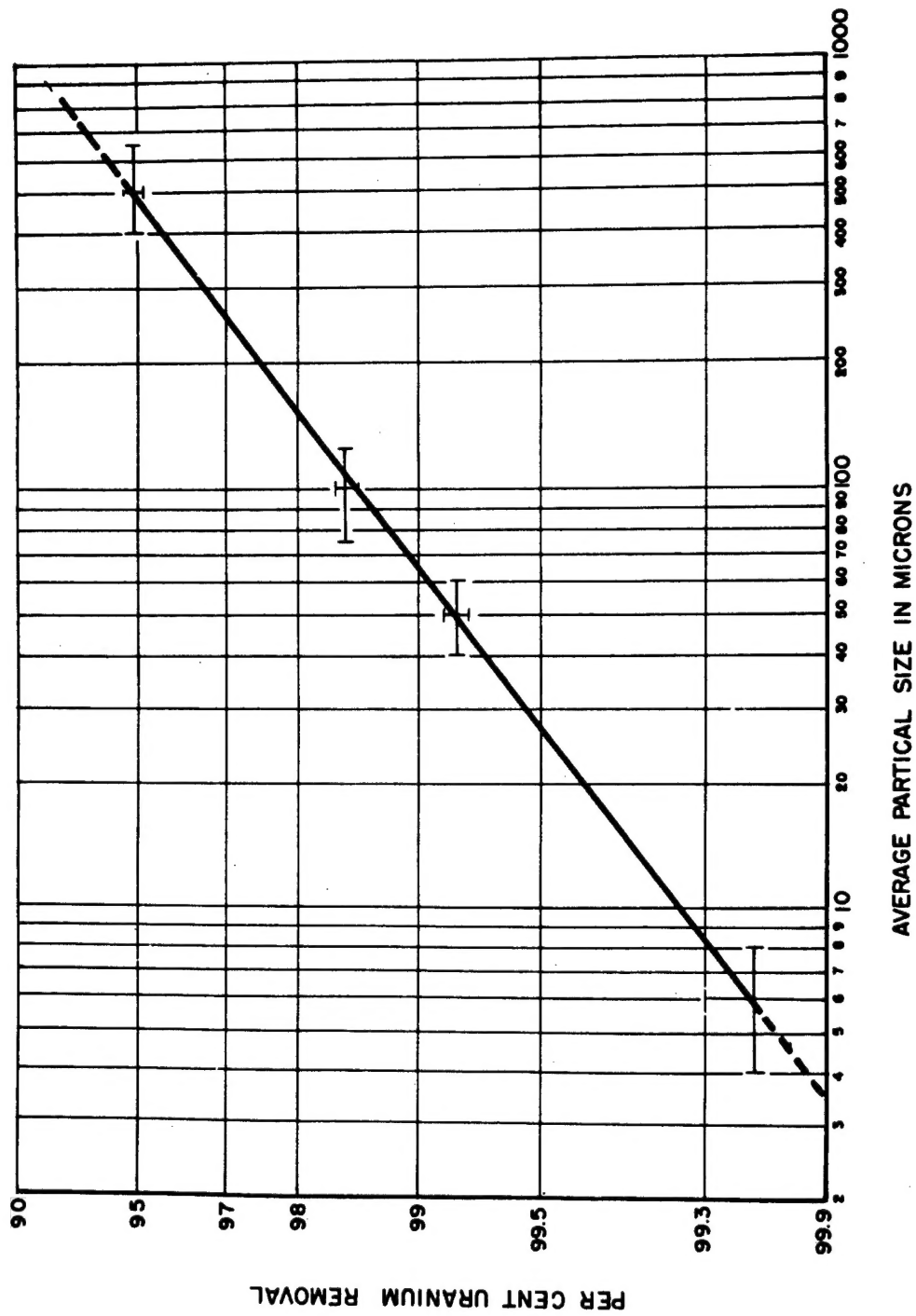| Sample Wt gm	Wt U gm	Reaction Time hr	Wt U Found in Residue gm	Wt U Collected gm	% Recovery Based on Residue	% Recovery Based on U Collected
0.317	0.181	3	0.0004	0.179	99.78	98.9
0.403	0.230	3	0.0006	0.224	99.74	97.4
0.248	0.1416	3	0.00025	0.1415	99.82	99.9
0.221	0.126	3	0.0002	0.123	99.84	97.5
0.170	0.0977	3	0.0001	0.098	99.90	100.3

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Figure 2.

Per Cent Uranium Recovery vs Average Particle Size

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